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THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

KLASEN, Melanie, et al.

Serial No. : 09/833,743

Filed : 4/13/01

For : LIQUID-CRYSTALLINE MEDIUM

SUBMISSION OF PRIORITY DOCUMENT(S)

Commissioner for Patents
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Sir:

Submitted herewith is a certified copy of each of the below-identified document(s), benefit of priority of each of which is claimed under 35 U.S.C. § 119:

| COUNTRY | APPLICATION NO. | FILING DATE |
|---------|-----------------|-------------|
| Germany | 100 18 899.0 | 4/14/00 |
| | | |

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Respectfully submitted,

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Date: January 20, 2004
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For and on behalf of RWS Group plc

The 17th day of December 2003

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**Priority Certificate
for the filing of a Patent Application**

File Reference: 100 18 899.0

Filing date: 14 April 2000

Applicant/Proprietor: Merck Patent GmbH, Darmstadt/DE

Title: Liquid-crystalline medium

IPC: C 09 K, G 02 F, G 09 F

The attached documents are a correct and accurate reproduction of the original submission for this Application.

Munich, 19 November 2003

German Patent and Trademark Office

The President

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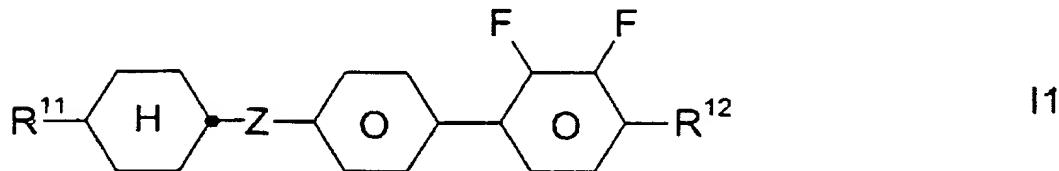
**Merck Patent Gesellschaft
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64271 Darmstadt

Liquid-crystalline medium

Liquid-crystallin medium

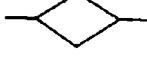
The invention relates to a liquid-crystalline medium based on a mixture of polar compounds having negative 5 dielectric anisotropy, which comprises at least one compound of the formula I1



and at least one compound of the formula I2



10 in which

15 R^{11} , R^{12} and R^{21} are each, independently of one another, an alkyl or alkenyl radical having up to 15 carbon atoms which is unsubstituted, monosubstituted by CN or CF_3 or at least 20 monosubstituted by halogen, where one or more CH_2 groups in these radicals may also, in each case independently of one another, be replaced by $-O-$, $-S-$, independently of one another by $-O-$, $-S-$, [sic]  $-C\equiv C-$, $-CO-$, $-CO-O-$, $-O-CO-$ or $-O-CO-O-$ in such a way that O atoms are not linked directly to one another,

25 Z is $-C_2H_4-$, $-CH=CH-$ or a single bond, and

30 alkenyl is a straight-chain alkenyl radical having 2-6 carbon atoms.

Such media are particularly suitable for electro-optical displays with active matrix addressing based on the ECB effect.

5 The principle of electrically controlled birefringence, the ECB effect or alternatively DAP effect (deformation of aligned phases), was described for the first time in 1971 (M.F. Schieckel and K. Fahrenschon, "Deformation of nematic liquid crystals with vertical orientation in 10 electrical fields", *Appl. Phys. Lett.* 19 (1971), 3912). This was followed by papers by J.F. Kahn (*Appl. Phys. Lett.* 20 (1972), 1193) and G. Labrunie and J. Robert (*J. Appl. Phys.* 44 (1973), 4869).

15 The papers by J. Robert and F. Clerc (SID 80 Digest Techn. Papers (1980), 30), J. Duchene (*Displays* 7 (1986), 3) and H. Schad (SID 82 Digest Techn. Papers (1982), 244) have shown that liquid-crystalline phases must have high values for the ratio between the elastic 20 constants K_3/K_1 , high values for the optical anisotropy Δn and values for the dielectric anisotropy $\Delta \epsilon$ of from -0.5 to -5 in order to be suitable for high-information display elements based on the ECB effect. Electro-optical display elements based on the ECB effect have a 25 homeotropic edge alignment.

Technical use of this effect in electro-optical display elements requires LC phases which must satisfy a multiplicity of requirements. Particularly important 30 here are chemical resistance to moisture, air and physical effects, such as heat, radiation in the infrared, visible and ultraviolet regions and direct and alternating electric fields.

35 Technically suitable LC phases are furthermore required to have a liquid-crystalline mesophase in a suitable temperature range and low viscosity.

None of the series of compounds having a liquid-crystalline mesophase which have been disclosed hitherto includes a single compound which meets all these requirements. In general, therefore, mixtures of 5 from 2 to 25, preferably from 3 to 18, compounds are prepared in order to obtain substances which can be used as LC phases. However, optimum phases could not be prepared easily in this way, since no liquid-crystalline materials of significantly negative 10 dielectric anisotropy were hitherto available.

Matrix liquid-crystal displays are known. Non-linear elements which can be used for individual switching of the individual pixels are, for example, active elements 15 (i.e. transistors). This is then referred to as an "active matrix", and a distinction can be made between two types:

1. MOS (metal oxide semiconductor) transistors on a 20 silicon wafer as substrate.
2. Thin-film transistors (TFTs) on a glass plate as substrate.

25 In the case of type 1, the electro-optical effect used is usually dynamic scattering or the guest-host effect. The use of single-crystal silicon as the substrate material limits the display size, since even modular assembly of various part-displays results in problems 30 at the joints.

In the case of more promising type 2, which is preferred, the electro-optical effect used is usually the TN effect.

35 A distinction is made between two technologies: TFTs comprising compound semiconductors, for example CdSe, or TFTs based on polycrystalline or amorphous silicon.

Intensive work is being carried out worldwide on the latter technology.

5 The TFT matrix is applied to the inside of one glass plate of the display, while the other glass plate carries the transparent counterelectrode on its inside. Compared with the size of the pixel electrode, the TFT is very small and has virtually no adverse effect on the image. This technology can also be expanded to 10 fully colour-compatible displays, in which a mosaic of red, green and blue filters is arranged in such a way that each filter element is located opposite a switchable pixel.

15 The TFT displays usually operate as TN cells with crossed polarizers in transmission and are backlit.

The term MLC displays here covers any matrix display containing integrated non-linear elements, i.e., 20 besides the active matrix, also displays containing passive elements, such as varistors or diodes (MIM = metal-insulator-metal).

MLC displays of this type are particularly suitable for 25 TV applications (for example pocket TVs) or for high-information displays in automobile or aircraft construction. Besides problems regarding the angle dependence of the contrast and the response times, difficulties also arise in MLC displays due to 30 inadequate resistivity of the liquid-crystal mixtures [TOGASHI, S., SEKIGUCHI, K., TANABE, H., YAMAMOTO, E., SORIMACHI, K., TAJIMA, E., WATANABE, H., SHIMIZU, H., Proc. Eurodisplay 84, Sept. 1984: A 210-288 Matrix LCD Controlled by Double Stage Diode Rings, p. 141 ff, 35 Paris; STROMER, M., Proc. Eurodisplay 84, Sept. 1984: Design of Thin Film Transistors for Matrix Addressing of Television Liquid Crystal Displays, p. 145 ff, Paris]. With decreasing resistance, the contrast of an MLC display drops. Since the resistivity of the liquid-

crystal mixture generally drops over the life of an MLC display owing to interaction with the interior surfaces of the display, a high (initial) resistance is very important for displays which must have acceptable 5 resistance values over a long service life.

The disadvantage of the MLC-TN displays disclosed hitherto is due to their comparatively low contrast, relatively high viewing-angle dependence and the 10 difficulty of generating grey shades in these displays.

EP 0 474 062 discloses MLC displays based on the ECB effect. However, the LC mixtures described therein, which are based on 2,3-difluorophenyl derivatives 15 containing an ester, ether or ethyl bridge, have low "voltage holding ratio" (HR) values after UV exposure.

There thus continues to be a great demand for MLC displays which have very high resistivity at the same 20 time as a broad operating temperature range, short response times and a low threshold voltage which can be used to produce various grey shades.

It is an object of the invention to provide MLC 25 displays based on the ECB effect which do not have the abovementioned disadvantages, or only do so to a lesser extent, and at the same time have very high resistivities.

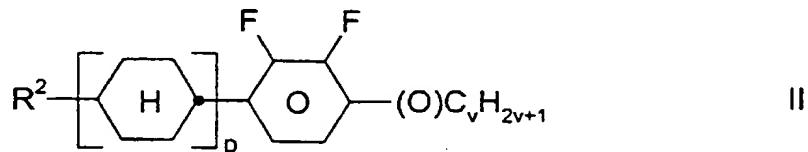
30 It has now been found that this object can be achieved if nematic liquid-crystal mixtures comprising at least one compound of the formula I1 and one compound of the formula I2 are used in these display elements.

35 The invention thus relates to a liquid-crystalline medium based on a mixture of polar compounds having negative dielectric anisotropy which comprises at least one compound of the formula I1 and at least one compound of the formula I2.

The mixture according to the invention has very favourable values for the capacitive threshold, relatively high values for the holding ratio and at the 5 same time very good low-temperature stability.

Some preferred embodiments are mentioned below:

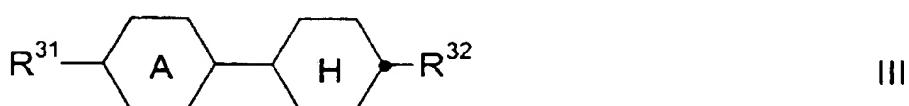
a) A medium which additionally comprises one or more 10 compounds of the formula II:



in which

15 R^2 is as defined for R^{11} , R^{12} and R^{21} ,
p is 1 or 2, and
20 v is from 1 to 6.

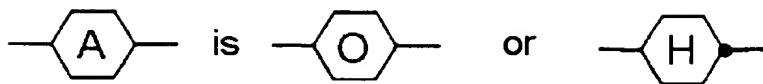
b) A medium which additionally comprises one or more compounds of the formula III:



25

in which

30 R^{31} and R^{32} are each, independently of one another, a straight-chain alkyl or alkyloxy radical having up to 12 carbon atoms, and



c) A medium which comprises two, three, four or more, preferably two, three or four, compounds of the formula II.

5

d) A medium which comprises at least two compounds of the formula I2.

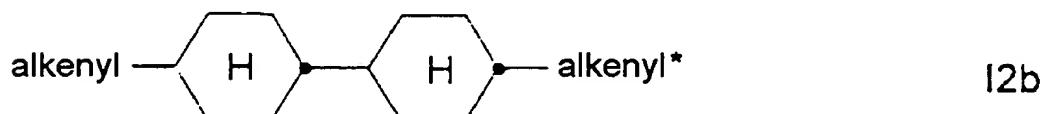
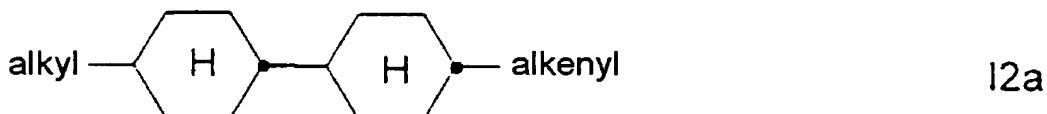
10 e) A medium in which the proportion of compounds of the formula II in the total mixture is at least 10% by weight, preferably at least 20% by weight.

15 f) A medium in which the proportion of compounds of the formula I2 in the total mixture is at least 5% by weight, preferably at least 10% by weight.

20 g) A medium in which the proportion of compounds of the formula II in the total mixture is at least 20% by weight.

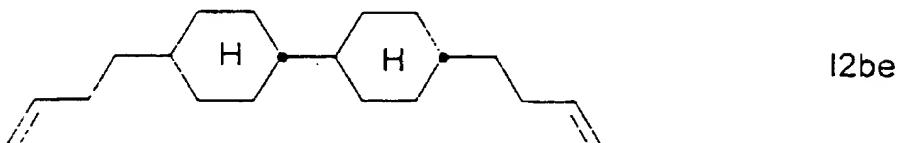
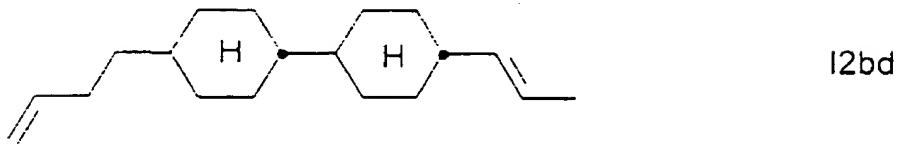
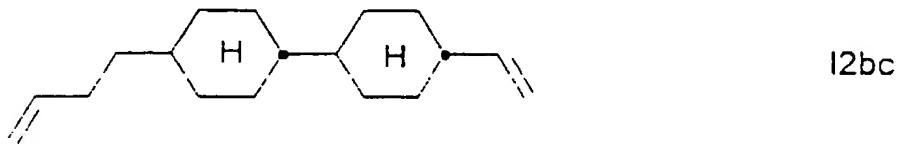
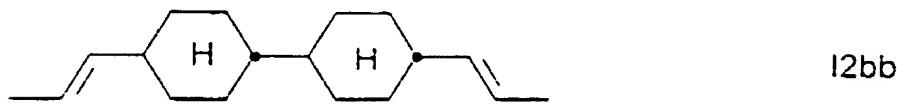
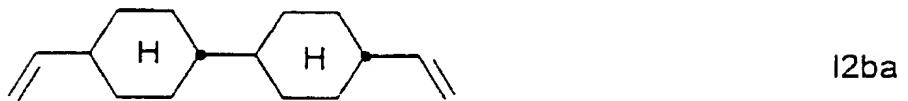
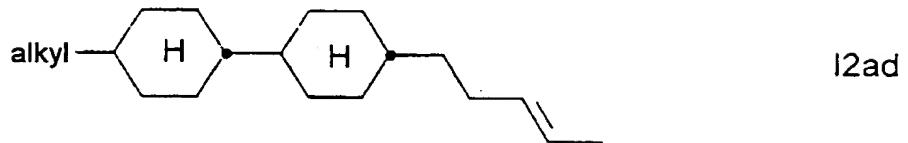
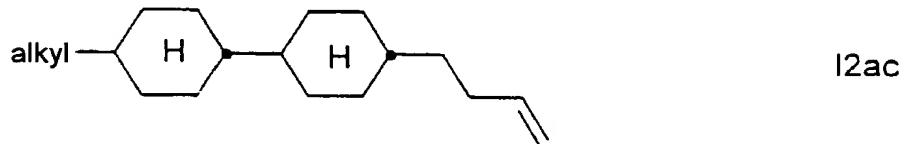
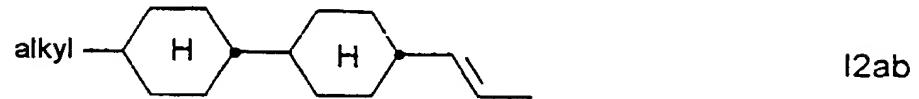
h) A medium in which the proportion of compounds of the formula III in the total mixture is at least 5% by weight.

25 i) A medium which comprises at least one compound selected from the formulae I2a and I2b.



Particular preference is given to the compounds of the formulae I2aa-I2ad and I2ba-I2be:

5



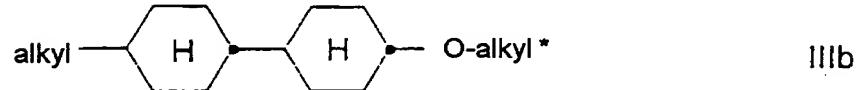
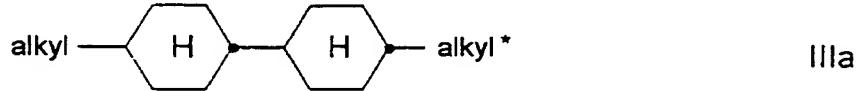
in which

alkenyl and
alkenyl* are each, independently of one another,
a straight-chain alkenyl radical having
2-6 carbon atoms, and

5

alkyl is a straight-chain alkyl radical having
1-6 carbon atoms.

10 j) A medium which additionally comprises a compound
selected from the formulae IIIa to IIId:



in which

15

alkyl and
alkyl* are each, independently of one another,
a straight-chain alkyl radical having
1-6 carbon atoms.

20

The medium according to the invention preferably
comprises at least one compound of the formula
IIIa and/or formula IIIb.

25

k) A medium which essentially consists of:

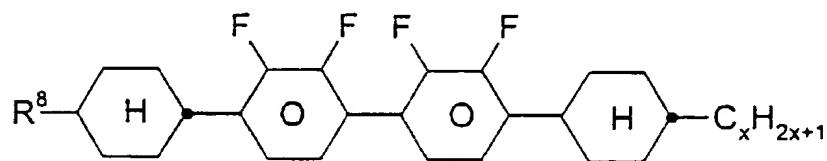
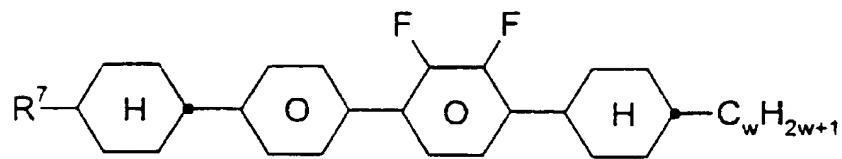
10-40% by weight of one or more compounds of the
formula II,

5-30% by weight of one or more compounds of the formula I2,

5 and

20-70% by weight of one or more compounds of the formula II.

10 1) A medium which additionally comprises one more compounds of the formulae

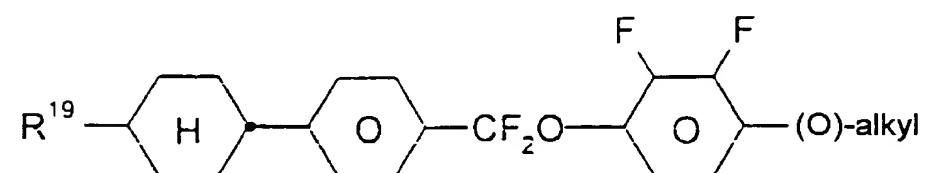
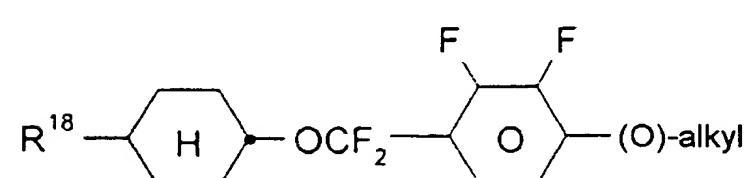
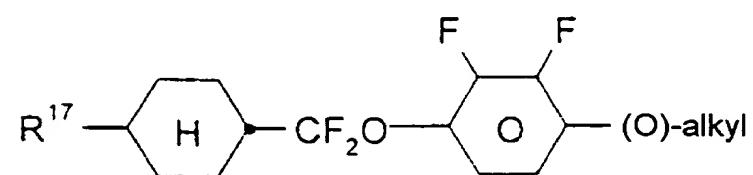
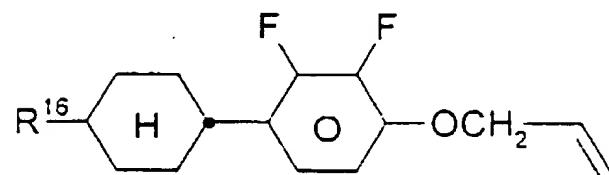
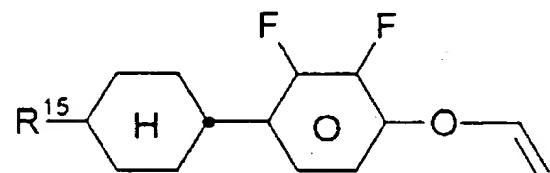
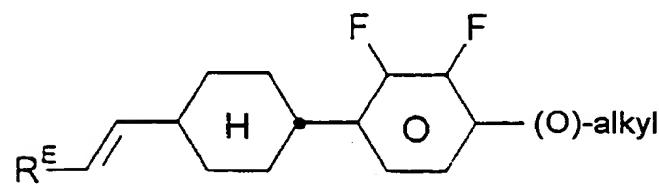
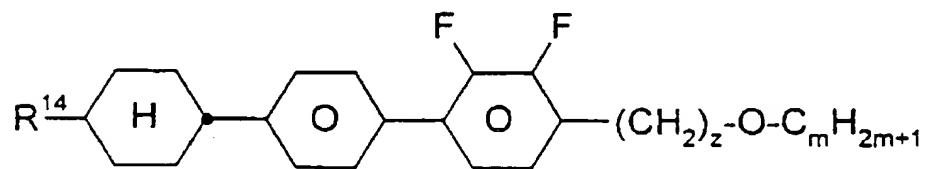
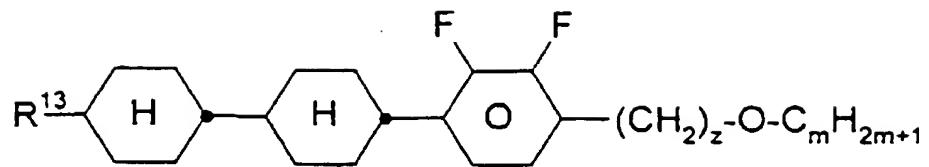


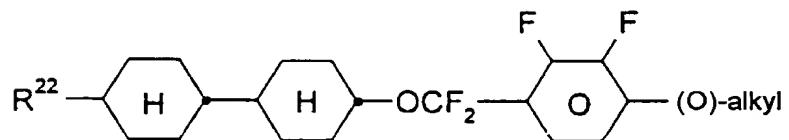
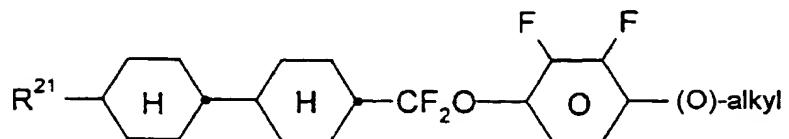
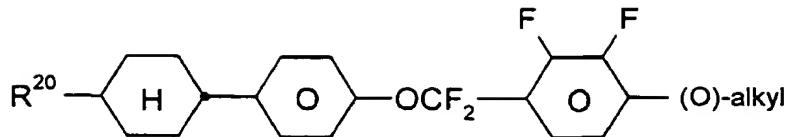
15 in which

20 R^7 and R^8 are each, independently of one another, as defined for R^{11} , R^{12} and R^{21} in Claim 1, and

w and x are each, independently of one another, from 1 to 6.

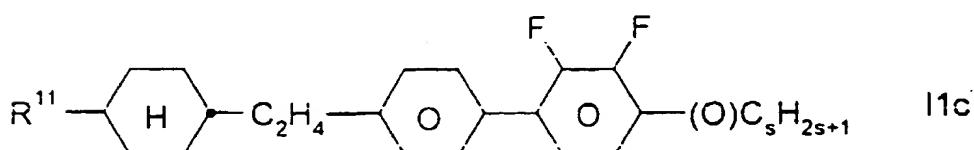
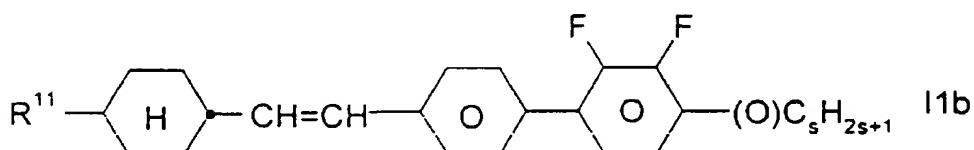
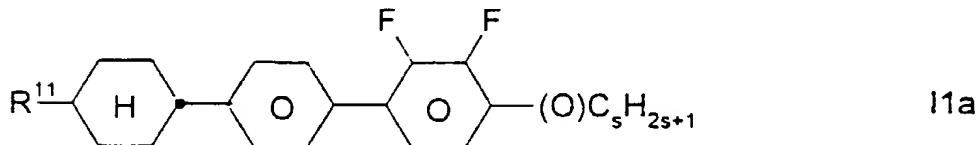
25 m) A medium which additionally comprises one more compounds of the formulae

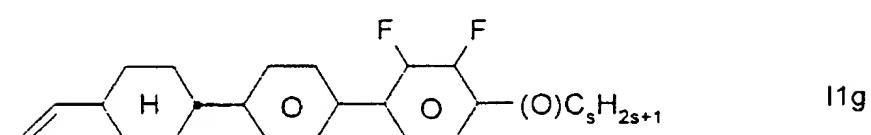
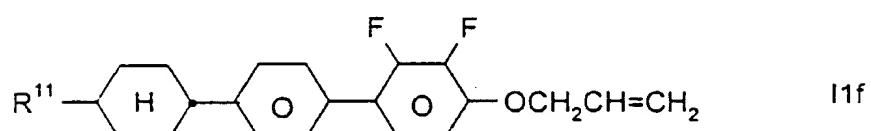
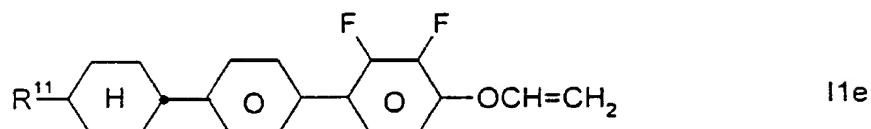
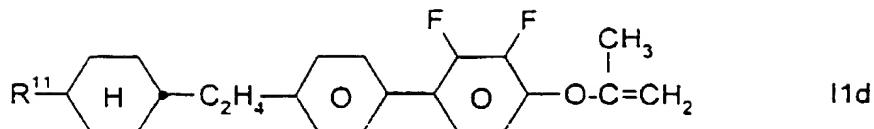




in which R^{13} - R^{22} are each, independently of one another, as defined for R^{11} , R^{12} and R^{21} , and z and m are each, independently of one another, 1-6. R^E is 5
H, CH_3 , C_2H_3 [sic] or $n\text{-C}_3\text{H}_7$.

n) A medium in which the compound of the formula I1 is selected from the group consisting of I1a to I1g:

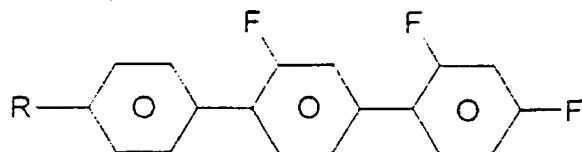




in which R^{11} is as defined in Claim 1, and s is 1-12. R^{11} is preferably straight-chain alkyl having 1 to 6 carbon atoms, vinyl, 1E-alkenyl or 3E-alkenyl.

- o) A medium which comprises one or more compounds of the formula IIa and/or IIg.

10 p) A medium which additionally comprises one or more compounds of the formula



15 in which R is alkyl, alkenyl, alkoxy, alkenyloxy
having 1 or 2 to 6 carbon atoms.

The invention furthermore relates to an electro-optical display having active matrix addressing based on the ECB effect, characterized in that it comprises, as dielectric, a liquid-crystalline medium according to one of Claims 1 to 13 [sic].

The liquid-crystal mixture preferably has a nematic phase range of at least 60 K and a maximum flow viscosity ν_{20} of 30 mm²·s⁻¹ at 20°C.

5

The liquid-crystal mixture according to the invention has a $\Delta\epsilon$ of from about -0.5 to -6.0, in particular from about -3.0 to -4.5, where $\Delta\epsilon$ is the dielectric anisotropy.

10 The rotational viscosity γ_1 is preferably < 225 mPa·s, in particular < 180 mPa·s.

The birefringence Δn in the liquid-crystal mixture is generally between 0.04 and 0.13, preferably between

15 0.06 and 0.11, and/or the dielectric constant $\epsilon_{||}$ of greater than or equal to 3, preferably from 3.2 to 8.5.

20 The dielectrics may also comprise further additives which are known to the person skilled in the art and are described in the literature.

For example, 0-15% of pleochroic dyes can be added, furthermore conductive salts, preferably ethyldimethyl-dodecylammonium 4-hexoxybenzoate, tetrabutylammonium

25 tetraphenylborate or complex salts of crown ethers (cf., for example, Haller et al., Mol. Cryst. Liq. Cryst., Volume 24, pages 249-258 (1973)) for improving the conductivity, or substances for modifying the dielectric anisotropy, the viscosity and/or the 30 alignment of the nematic phases. Such substances are described, for example, in DE-A 22 09 127, 22 40 864, 23 21 632, 23 38 281, 24 50 088, 26 37 430 and 28 53 728.

35 The individual components of the formulae I1, I2, II and III in the liquid-crystal phases according to the invention are either known or their modes of preparation can easily be derived from the prior art by the person skilled in the relevant art, since they are

based on standard methods which are described in the literature.

5 The nematic liquid-crystal mixtures in the displays according to the invention generally comprise two components A and B, which themselves consist of one or more individual compounds.

10 Component A has significantly negative dielectric anisotropy and gives the nematic phase a dielectric anisotropy of ≤ -0.3 . It preferably comprises compounds of the formulae I1 and II.

15 The proportion of component A is preferably between 45 and 100%, in particular between 60 and 100%.

20 For component A, one (or more) individual compound(s) having a $\Delta\epsilon \leq -0.8$ are preferably selected. The smaller the proportion of component A in the total mixture, the more negative this value must be.

Component B has pronounced nematogeneity and a flow viscosity of not more than $30 \text{ mm}^2 \cdot \text{s}^{-1}$, preferably not more than $25 \text{ mm}^2 \cdot \text{s}^{-1}$, at 20°C .

25 Particularly preferred individual compounds of component B are extremely low-viscosity nematic liquid crystals having a flow viscosity of not more than $18 \text{ mm}^2 \cdot \text{s}^{-1}$, preferably not more than $12 \text{ mm}^2 \cdot \text{s}^{-1}$, at 20°C .

30 Component B has monotropic or enantiotropic nematogeneity, has no smectic phases and can prevent the occurrence of smectic phases in liquid-crystal mixtures down to very low temperatures. If, for 35 example, a smectic liquid-crystal mixture is mixed with various materials of high nematogeneity, the degree of suppression of smectic phases that is achieved can be used to compare the nematogeneity of these materials.

Numerous suitable materials are known to the person skilled in the art from the literature. Particular preference is given to compounds of the formula III.

5 In addition, these liquid-crystal phases can also contain more than 18 components, preferably from 18 to 25 components.

10 The phases preferably contain from 4 to 15, in particular 5 to 12, compounds of the formulae I1, I2, II and optionally III.

15 Besides compounds of the formulae I1, I2, II and III, it is also possible for other constituents to be present, for example in an amount of up to 45% of the total mixture, but preferably up to 35%, in particular up to 10%.

20 The other constituents are preferably selected from nematic or nematogenic substances, in particular known substances, from the classes consisting of the azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexyl-naphthalenes, 1,4-bis-cyclohexylbiphenyls or cyclohexyl-pyrimidines, phenyl- or cyclohexyldioxanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolans and substituted cinnamic acids.

25 30 The most important compounds which can be used as constituents of liquid-crystal mixtures of this type can be characterized by the formula IV

35 $R^9-L-G-E-R^{10}$ IV

in which L and E are each a carbocyclic or heterocyclic ring system from the group consisting of 1,4-disubstituted benzene and cyclohexane rings, 4,4'-

disubstituted biphenyl, phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, di- and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline,

| | | |
|------|---------|-------------------------------------|
| G is | -CH=CH- | -N(O)=N- |
| | -CH-CQ- | -CH=N(O)- |
| | -C≡C- | -CH ₂ -CH ₂ - |
| 10 | -CO-O- | -CH ₂ -O- |
| | -CO-S- | -CH ₂ -S- |
| | -CH=N- | -COO-Phe-COO- |

or a C-C single bond, Q is halogen, preferably chlorine, 15 or -CN, and R⁹ and R¹⁰ are each alkyl, alkenyl, alkoxy, alkanoyloxy or alkoxy carbonyloxy having up to 18, preferably up to 8, carbon atoms, or one of these radicals is alternatively CN, NC, NO₂, NCS, CF₃, F, Cl or Br.

20 In most of these compounds, R⁹ and R¹⁰ are different from one another, one of these radicals usually being an alkyl or alkoxy group. However, other variants of the proposed substituents are also common. Many such 25 substances or mixtures thereof are commercially available. All these substances can be prepared by methods which are known from the literature.

30 It will be appreciated by a person skilled in the art that the ECB mixture according to the invention may also comprise compounds in which, for example, H, N, O, Cl or F have been replaced by the corresponding isotopes.

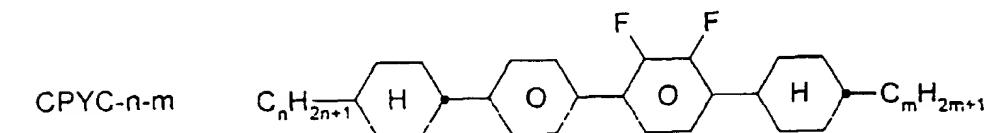
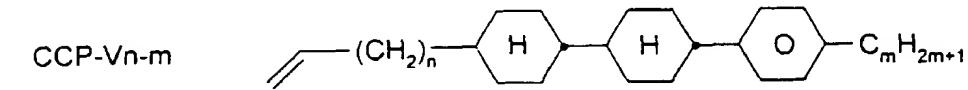
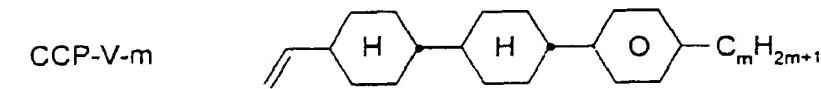
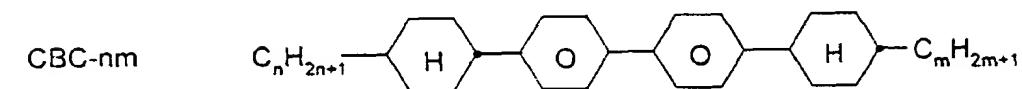
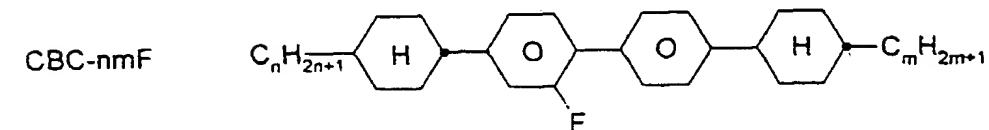
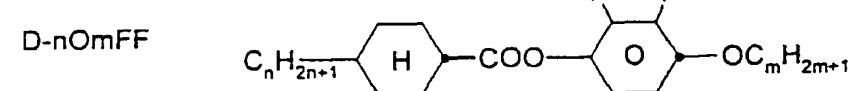
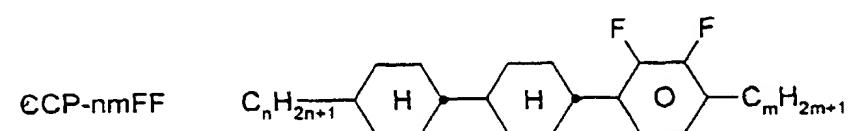
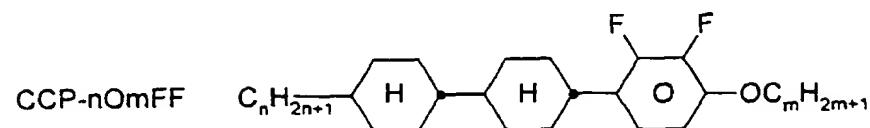
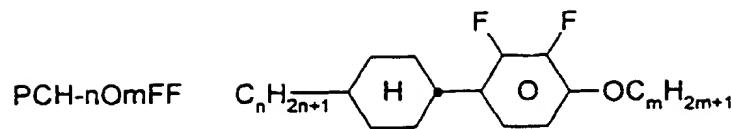
35 The construction of the liquid-crystal displays according to the invention corresponds to the conventional geometry, as described, for example, in EP-A 0 240 379.

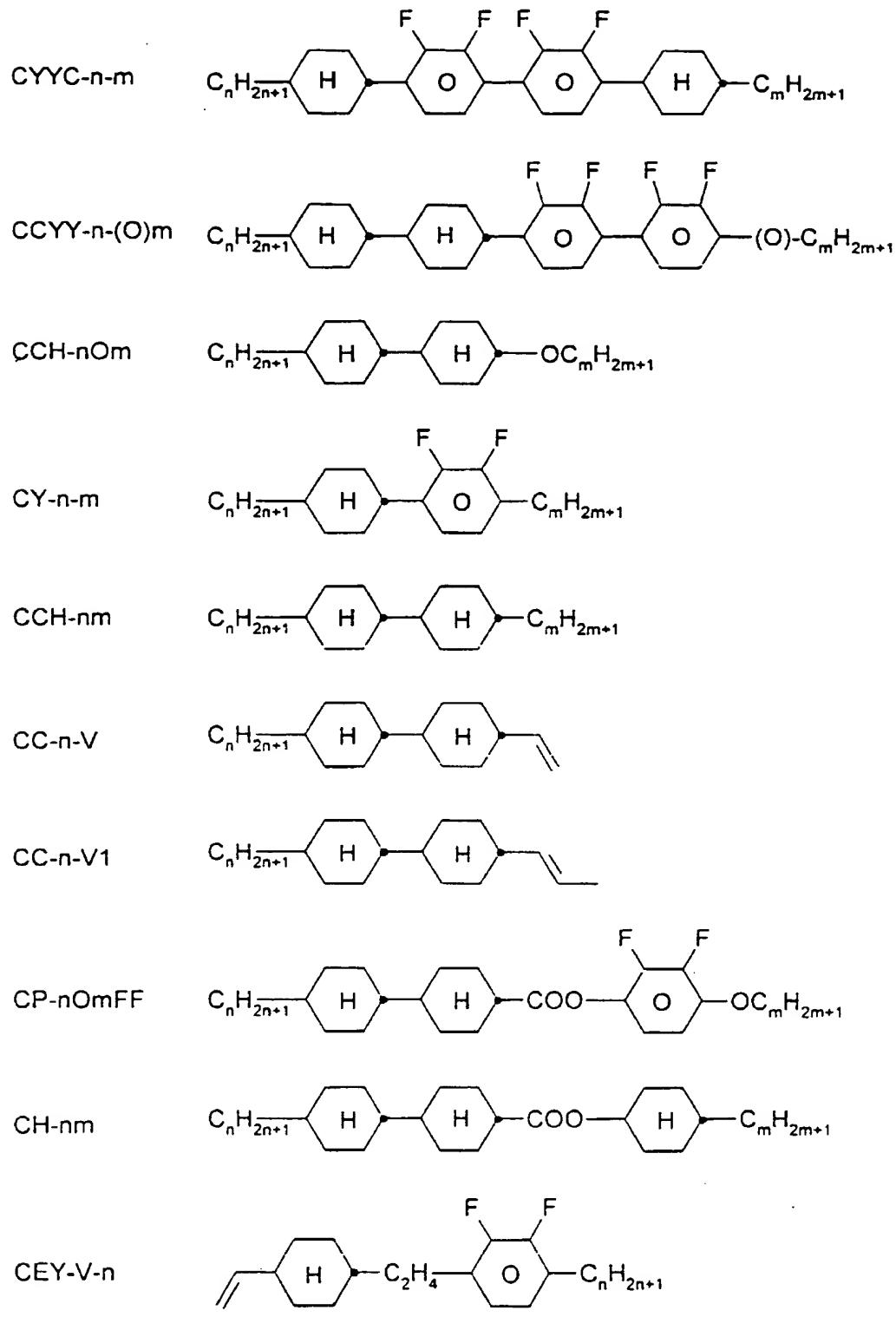
The examples below are intended to illustrate the invention without limiting it. Hereinbefore and hereinafter, percentages are given in per cent by weight; all temperatures are specified in degrees 5 Celsius.

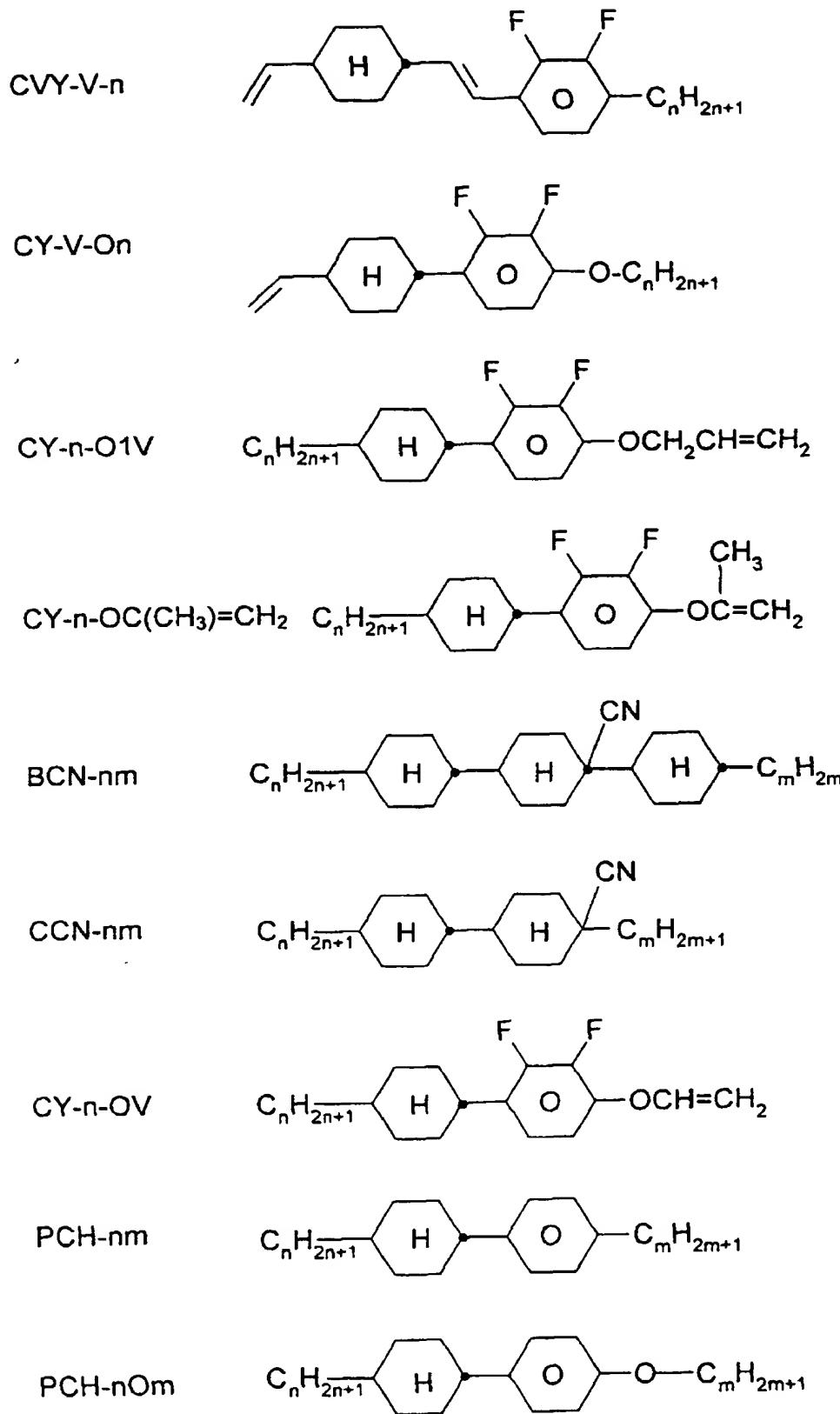
Besides the compounds of the formulae I1 and I2, the liquid-crystal mixtures according to the invention preferably comprise one or more of the compounds 10 mentioned below.

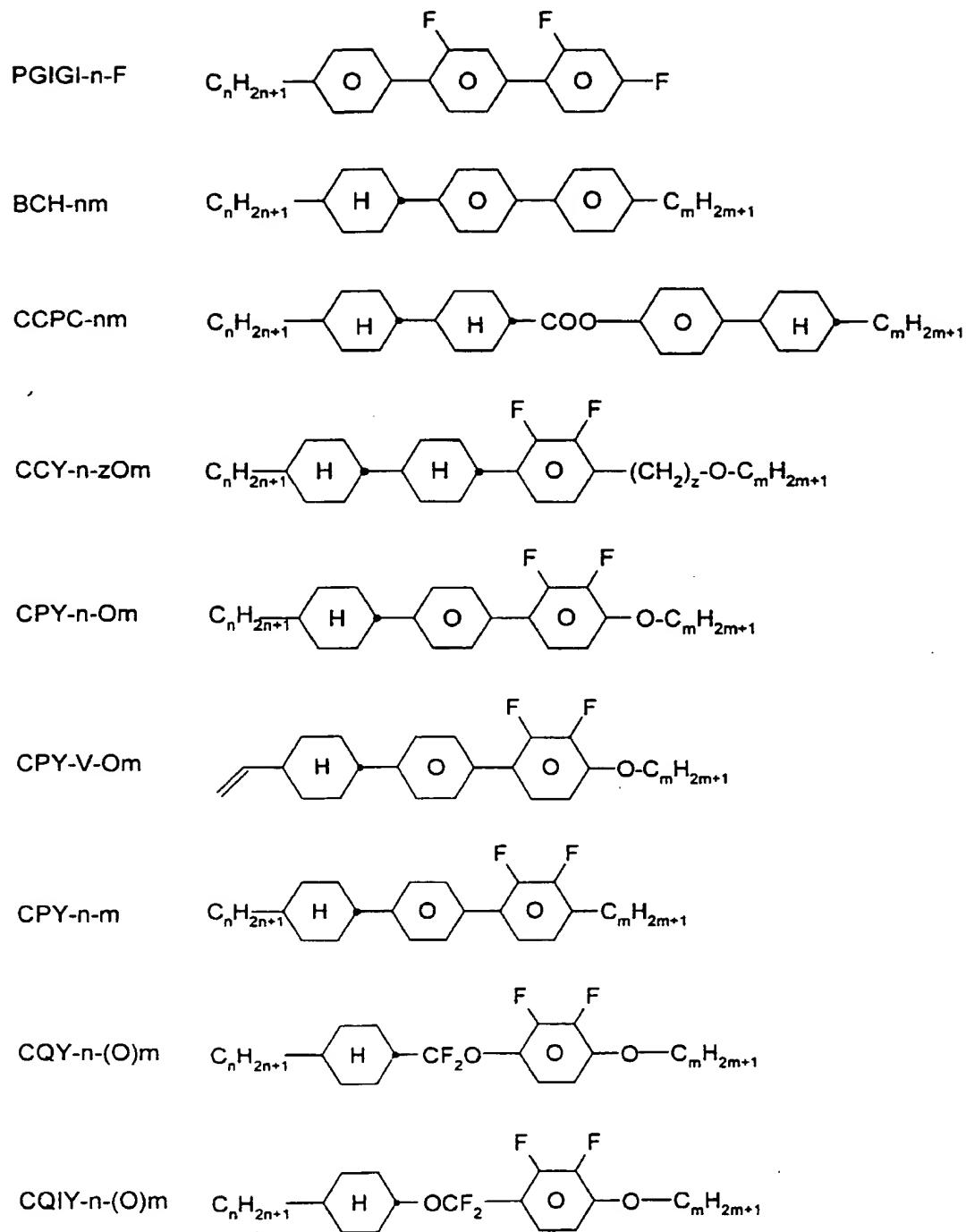
The following abbreviations are used:

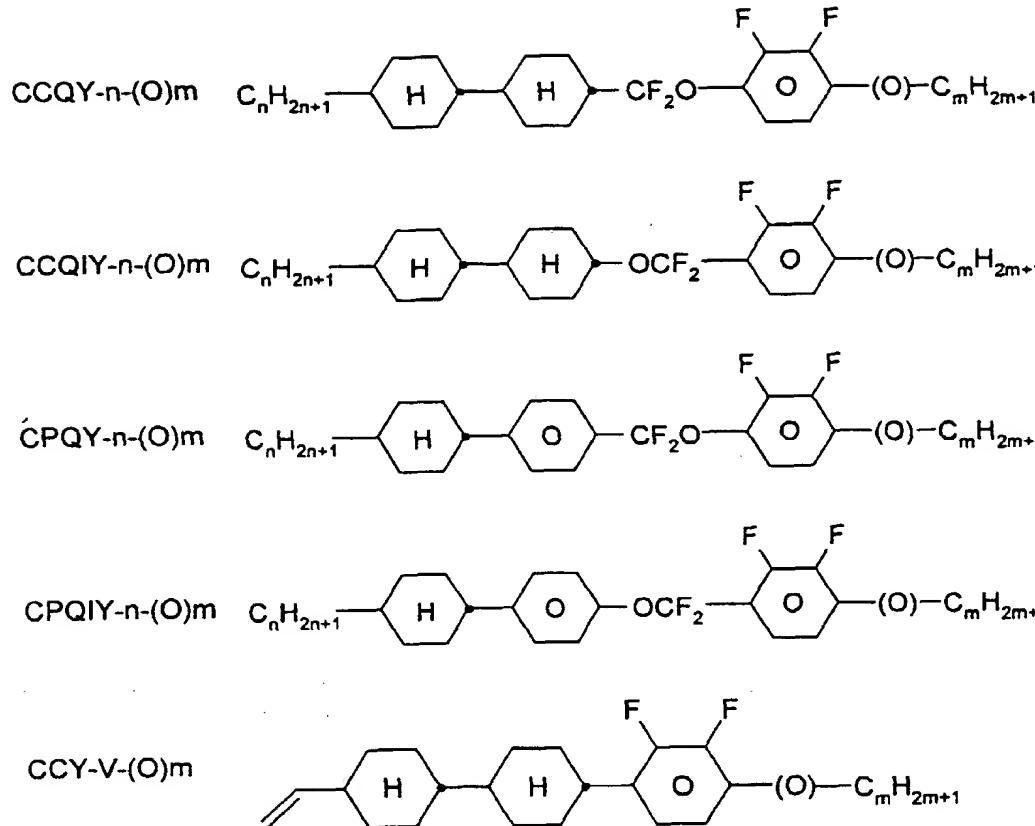
(n, m = 1-6; z = 1-6)











The abbreviations furthermore have the following meanings:

5 V_o threshold voltage, capacitive [V] at 20°C

Δn optical anisotropy measured at 20°C and 589 nm

Δε dielectric anisotropy at 20°C and 1 kHz

10

c.p. clearing point [°C]

γ₁ rotational viscosity measured at 20°C [mPa·s]

15 LTS low temperature stability

The display used to measure the threshold voltage has two plane-parallel outer plates at a separation of 5 μm and electrode layers covered by lecithin alignment

20 layers on the inside of the outer plates, which produce a homeotropic alignment of the liquid crystal molecules.

Mixture examples

Example 1

5

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 18.0% | $S \rightarrow N:$ | < -40°C |
| PCH-504FF | 19.0% | Clearing point [°C]: | 69.5 |
| BCH-32 | 8.0% | Δn [589 nm, 20°C]: | +0.1011 |
| CCP-V-1 | 7.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -3.3 |
| CC-3-V1 | 8.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.6 |
| CC-5-V | 18.0% | γ_1 [mPa·s, 20°C]: | 115 |
| CPY-2-02 | 12.0% | V_o [V]: | 2.10 |
| CPY-3-02 | 10.0% | LTS in cells: nem. > | 1 000 h |
| | | At -20°C, -30°C, -40°C | |

Example 2

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 19.0% | $S \rightarrow N:$ | < -40°C |
| PCH-504FF | 20.0% | Clearing point [°C]: | 71.0 |
| CCP-302FF | 6.0% | Δn [589 nm, 20°C]: | +0.1020 |
| BCH-32 | 7.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -3.9 |
| CCH-35 | 5.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.7 |
| CC-3-V1 | 8.0% | γ_1 [mPa·s, 20°C]: | 142 |
| CC-5-V | 11.0% | V_o [V]: | 1.92 |
| CPY-2-02 | 12.0% | LTS in cells: nem. > | 1 000 h |
| CPY-3-02 | 12.0% | At -20°C and -30°C | |

10 Example 3

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 10.0% | $S \rightarrow N:$ | < -30°C |
| PCH-502FF | 8.0% | Clearing point [°C]: | 75.5 |
| PCH-504FF | 18.0% | Δn [589 nm, 20°C]: | +0.1005 |
| CCP-302FF | 10.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -4.2 |
| CC-3-V1 | 8.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.7 |
| CC-5-V | 13.0% | γ_1 [mPa·s, 20°C]: | 149 |
| CCH-35 | 5.0% | V_o [V]: | 1.95 |
| CPY-2-02 | 12.0% | | |
| CPY-3-02 | 12.0% | | |
| BCH-32 | 4.0% | | |

Example 4

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 8.0% | $S \rightarrow N:$ | < -30°C |
| PCH-502FF | 8.0% | Clearing point [°C]: | 83.5 |
| PCH-504FF | 18.0% | Δn [589 nm, 20°C]: | +0.1022 |
| CCP-302FF | 14.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -4.9 |
| CCP-31FF | 7.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.8 |
| CC-5-V | 8.0% | γ_1 [mPa·s, 20°C]: | 189 |
| CC-3-V1 | 8.0% | V_o [V]: | 1.93 |
| CCH-35 | 5.0% | | |
| CPY-2-02 | 12.0% | | |
| CPY-3-02 | 12.0% | | |

Example 5

5

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 11.0% | $S \rightarrow N:$ | < -30°C |
| PCH-504FF | 16.0% | Clearing point [°C]: | 83.5 |
| CC-5-V | 12.0% | Δn [589 nm, 20°C]: | +0.1006 |
| PCH-302 | 6.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -3.7 |
| CCH-35 | 5.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.5 |
| CC-3-V1 | 8.0% | γ_1 [mPa·s, 20°C]: | 150 |
| CPY-2-02 | 12.0% | V_o [V]: | 2.23 |
| CPY-3-02 | 12.0% | | |
| CCP-302FF | 11.0% | | |
| CCP-V2-1 | 7.0% | | |

Example 6

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-502FF | 8.0% | $S \rightarrow N:$ | < -30°C |
| PCH-504FF | 16.0% | Clearing point [°C]: | 70.5 |
| PCH-301 | 9.0% | Δn [589 nm, 20°C]: | +0.1007 |
| CCP-V2-1 | 5.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -4.2 |
| CC-3-V1 | 9.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.9 |
| CCH-35 | 5.0% | γ_1 [mPa·s, 20°C]: | 139 |
| CC-5-V | 6.0% | V_o [V]: | 1.96 |
| D-302-FF | 8.0% | | |
| D-502FF | 8.0% | | |
| CPY-2-02 | 14.0% | | |
| CPY-3-02 | 12.0% | | |

Example 7

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 14.0% | $S \rightarrow N:$ | < -30°C |
| PCH-502FF | 7.0% | Clearing point [°C]: | 80.5 |
| PCH-504FF | 18.0% | Δn [589 nm, 20°C]: | +0.1006 |
| CC-5-V | 8.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -4.9 |
| CC-3-V1 | 8.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.8 |
| CCH-35 | 5.0% | γ_1 [mPa·s, 20°C]: | 186 |
| CPY-2-02 | 12.0% | V_o [V]: | 1.89 |
| CPY-3-02 | 12.0% | | |
| CCP-302FF | 13.0% | | |
| CCPC-33 | 3.0% | | |

Example 8

5

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 14.0% | $S \rightarrow N:$ | < -30°C |
| PCH-502FF | 10.0% | Clearing point [°C]: | 80.0 |
| PCH-504FF | 17.0% | Δn [589 nm, 20°C]: | +0.1104 |
| CCH-35 | 5.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -5.1 |
| CC-3-V1 | 9.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.8 |
| BCH-32 | 6.0% | γ_1 [mPa·s, 20°C]: | 202 |
| CPY-2-02 | 13.0% | V_o [V]: | 1.83 |
| CPY-3-02 | 12.0% | | |
| CCP-302FF | 14.0% | | |

Example 9

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 14.0% | $S \rightarrow N:$ | < -30°C |
| PCH-502FF | 8.0% | Clearing point [°C]: | 70.0 |
| PCH-504FF | 15.0% | Δn [589 nm, 20°C]: | +0.0906 |
| CCP-302FF | 8.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -3.7 |
| CPY-2-02 | 9.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.6 |
| CPY-3-02 | 10.0% | γ_1 [mPa·s, 20°C]: | 119 |
| CCP-V2-1 | 5.0% | V_o [V]: | 2.03 |
| CC-3-V1 | 8.0% | | |
| CCH-35 | 5.0% | | |
| CC-5-V | 18.0% | | |

Example 10

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 18.0% | $S \rightarrow N:$ | < -30°C |
| PCH-502FF | 10.0% | Clearing point [°C]: | 80.5 |
| PCH-504FF | 15.0% | Δn [589 nm, 20°C]: | +0.1192 |
| CCP-302FF | 10.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -5.1 |
| BCH-32 | 8.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 4.0 |
| CCP-V-1 | 10.0% | γ_1 [mPa·s, 20°C]: | 225 |
| PCH-302 | 3.0% | V_o [V]: | 1.83 |
| PGIGI-3-F | 2.0% | | |
| CPY-2-02 | 12.0% | | |
| CPY-3-02 | 12.0% | | |

Example 11

5

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 15.0% | $S \rightarrow N:$ | < -30°C |
| PCH-504FF | 15.0% | Clearing point [°C]: | 79.0 |
| CCH-35 | 5.0% | Δn [589 nm, 20°C]: | +0.1122 |
| CC-5-V | 12.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -3.7 |
| CC-3-V1 | 10.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.6 |
| BCH-32 | 8.0% | V_o [V]: | 2.04 |
| CPY-2-02 | 10.0% | γ_1 [mPa·s, 20°C]: | 145 |
| CPY-3-02 | 7.0% | | |
| CPY-V-02 | 10.0% | | |
| CPY-V-04 | 8.0% | | |

Example 12

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 10.0% | $S \rightarrow N:$ | < -30°C |
| PCH-504FF | 16.0% | Clearing point [°C]: | 80.0 |
| CCH-35 | 5.0% | Δn [589 nm, 20°C]: | +0.1021 |
| CC-5-V | 20.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -3.5 |
| CC-3-V1 | 10.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.5 |
| BCH-32 | 3.0% | V_o [V]: | 2.17 |
| CPY-2-02 | 10.0% | γ_1 [mPa·s, 20°C]: | 131 |
| CPY-3-02 | 10.0% | LTS in cells: nem. > | 1 000 h |
| CPY-V-02 | 10.0% | at -20°C, -30°C | |
| CCP-302FF | 6.0% | | |

Example 13

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 14.0% | $S \rightarrow N:$ | < -30°C |
| PCH-504FF | 15.0% | Clearing point [°C]: | 84.0 |
| CCY-V-02 | 10.0% | Δn [589 nm, 20°C]: | +0.1140 |
| CPY-3-1 | 9.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -4.8 |
| CC-3-V1 | 10.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.8 |
| CCH-35 | 5.0% | V_o [V]: | 1.94 |
| CC-5-V | 7.0% | γ_1 [mPa·s, 20°C]: | 183 |
| CPY-V-02 | 10.0% | LTS in cells: nem. > | 1 000 h |
| CPY-2-02 | 10.0% | at -20°C | |
| CPY-3-02 | 10.0% | | |

Example 14

5

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 20.0% | $S \rightarrow N:$ | < -40°C |
| PCH-504FF | 16.0% | Clearing point [°C]: | 69.0 |
| BCH-32 | 8.0% | Δn [589 nm, 20°C]: | +0.0978 |
| CCP-V-1 | 8.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -3.0 |
| CC-3-V1 | 8.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.6 |
| CC-5-V | 20.0% | V_o [V]: | 2.17 |
| CPY-2-02 | 10.0% | γ_1 [mPa·s, 20°C]: | 108 |
| CPY-3-02 | 10.0% | LTS in cells: nem. > | 1 000 h |
| | | at -20°C, -30°C, -40°C | |

Example 15

| | | | |
|-----------|-------|----------------------------------|---------|
| PCH-304FF | 16.0% | $S \rightarrow N:$ | < -30°C |
| PCH-504FF | 18.0% | Clearing point [°C]: | 73.5 |
| CCP-302FF | 6.0% | Δn [589 nm, 20°C]: | +0.0883 |
| CPY-2-02 | 6.0% | $\Delta \epsilon$ [1 kHz, 20°C]: | -3.1 |
| CPY-3-02 | 11.0% | $\epsilon_{ }$ [1 kHz, 20°C]: | 3.4 |
| CCP-V2-1 | 10.0% | V_o [V]: | 2.26 |
| CC-3-V12 | 8.0% | γ_1 [mPa·s, 20°C]: | 113 |
| CCH-35 | 5.0% | LTS in cells: nem. > | 1 000 h |
| CC-5-V | 20.0% | at -20°C and -30°C | |

Example 16

| | | | |
|------------|-------|--------------------------------|----------|
| PCH-304FF | 13.0% | Clearing point [°C]: | 70 |
| PCH-502FF | 8.0% | Δn [589 nm, 20°C]: | + 0.0986 |
| PCH-504FF | 11.0% | Δε [1 kHz, 20°C]: | -3.2 |
| CPY-3-02 | 10.0% | ε [1 kHz, 20°C]: | 3.6 |
| CPQIY-3-02 | 5.0% | V _o [V]: | 2.12 |
| CPQIY-3-04 | 5.0% | γ ₁ [mPa·s, 20°C]: | 116 |
| CPY-2-02 | 9.0% | | |
| BCH-32 | 8.0% | | |
| CC-3-V1 | 8.0% | | |
| CCH-35 | 5.0% | | |
| CC-5-V | 18.0% | | |

Example 17

| | | | |
|-----------|-------|--------------------------------|----------|
| PCH-304FF | 16.0% | Clearing point [°C]: | 70.5 |
| PCH-502FF | 8.0% | Δn [589 nm, 20°C]: | + 0.0954 |
| PCH-504FF | 12.0% | Δε [1 kHz, 20°C]: | -3.4 |
| CPY-3-02 | 8.0% | ε [1 kHz, 20°C]: | 3.6 |
| CCQY-3-02 | 5.0% | V _o [V]: | 2.08 |
| CCQY-5-02 | 5.0% | γ ₁ [mPa·s, 20°C]: | 122 |
| CPY-2-02 | 9.0% | | |
| BCH-32 | 8.0% | | |
| CC-3-V1 | 8.0% | | |
| CCH-35 | 5.0% | | |
| CC-5-V | 16.0% | | |

Example 18

| | | | |
|-----------|-------|--------------------------------|----------|
| PCH-304FF | 8.0% | Clearing point [°C]: | 70.0 |
| PCH-502FF | 10.0% | Δn [589 nm, 20°C]: | + 0.1023 |
| PCH-504FF | 14.0% | Δε [1 kHz, 20°C]: | -3.3 |
| CPY-3-02 | 12.0% | ε [1 kHz, 20°C]: | 3.6 |
| CQY-5-1 | 5.0% | V _o [V]: | 2.14 |
| CQY-5-02 | 5.0% | γ ₁ [mPa·s, 20°C]: | 104 |
| CPY-3-04 | 12.0% | | |
| BCH-32 | 9.0% | | |
| CC-3-V1 | 10.0% | | |
| CCH-35 | 5.0% | | |
| CC-5-V | 10.0% | | |

Example 19

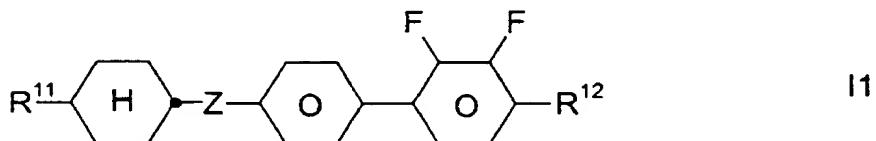
| | | | |
|------------|-------|--------------------------------|----------|
| PCH-304FF | 11.0% | Clearing point [°C]: | 69.5 |
| PCH-502FF | 9.0% | Δn [589 nm, 20°C]: | + 0.0952 |
| PCH-504FF | 16.0% | Δε [1 kHz, 20°C]: | -3.6 |
| CPQIY-3-02 | 8.0% | ε [1 kHz, 20°C]: | 3.6 |
| CPY-2-04 | 10.0% | V _o [V]: | 2.08 |
| CPY-3-02 | 11.0% | γ ₁ [mPa·s, 20°C]: | 120 |
| CCPC-33 | 3.0% | | |
| CC-3-V1 | 8.0% | | |
| CCH-35 | 5.0% | | |
| CC-5-V | 19.0% | | |

5 Example 20

| | | | |
|-----------|-------|--------------------------------|----------|
| PCH-304FF | 13.0% | Clearing point [°C]: | 70.5 |
| PCH-502FF | 8.0% | Δn [589 nm, 20°C]: | + 0.0900 |
| PCH-504FF | 16.0% | Δε [1 kHz, 20°C]: | -3.7 |
| CPQY-3-02 | 8.0% | ε [1 kHz, 20°C]: | 3.6 |
| CPY-2-02 | 10.0% | V _o [V]: | 2.06 |
| CPY-3-02 | 10.0% | γ ₁ [mPa·s, 20°C]: | 119 |
| CCP-V2-1 | 4.0% | | |
| CC-3-V1 | 8.0% | | |
| CCH-35 | 5.0% | | |
| CC-5-V | 18.0% | | |

Patent Claims

1. Liquid-crystalline medium based on a mixture of polar compounds having negative dielectric anisotropy, characterized in that it comprises at least one compound of the formula I1



and at least one compound of the formula I2



in which

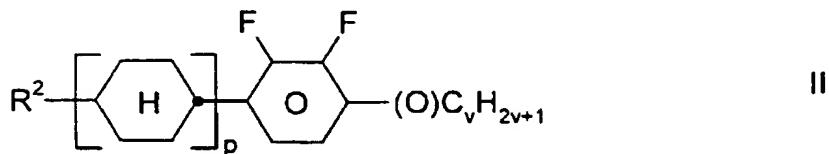
R¹¹, R¹² and R²¹ are each, independently of one another, an alkyl or alkenyl radical having up to 15 carbon atoms which is unsubstituted, monosubstituted by CN or CF₃ or at least monosubstituted by halogen, where one or more CH₂ groups in these radicals may also, in each case independently of one another, be replaced by -O-, -S-, independently of one another by -O-, -S-, [sic], , -C≡C-, -CO-, -CO-O-, O-CO- or -O-CO-O- in such a way that O atoms are not linked directly to one another,

Z is $-C_2H_4-$, $-CH=CH-$ or a single bond, and

5 alkenyl is a straight-chain alkenyl radical having 2-6 carbon atoms.

2. Medium according to Claim 1, characterized in that it additionally comprises one or more compounds of the formula II

10



in which

15 R^2 is as defined for R^{11} , R^{12} and R^{21} .

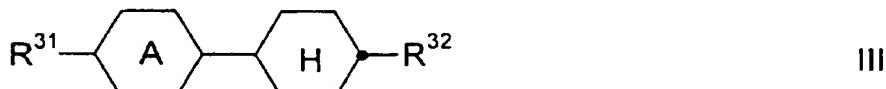
p is 1 or 2, and

v is from 1 to 6.

20

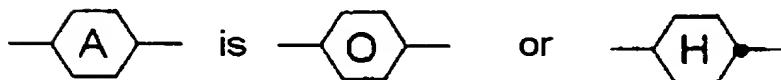
3. Medium according to Claim 1 or 2, characterized in that it additionally comprises one or more compounds of the formula III

25

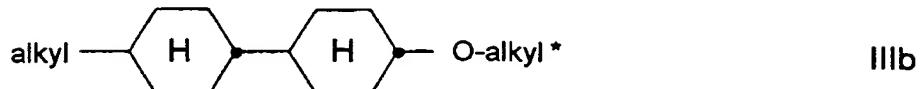
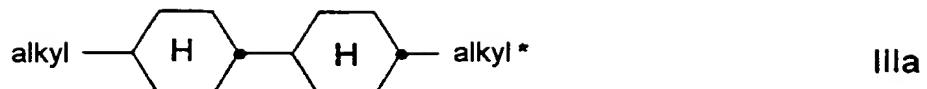


in which

30 R^{31} and R^{32} are each, independently of one another, a straight-chain alkyl or alkyloxy radical having 1-12 carbon atoms, and



4. Medium according to at least one of Claims 1 to 3, characterized in that it essentially contains [sic] of three, four or more compounds selected from the formulae I1 and I2.
5. Medium according to one of Claims 1 to 4, characterized in that the proportion of compounds of the formula I1 in the total mixture is at least 10% by weight.
10. Medium according to one of Claims 1 to 5, characterized in that the proportion of compounds of the formula I2 in the total mixture is at least 5% by weight.
15. Medium according to one of Claims 1 to 6, characterized in that the proportion of compounds of the formula II in the total mixture is at least 20% by weight.
20. Medium according to one of Claims 1 to 7, characterized in that the proportion of compounds of the formula III in the total mixture is at least 5% by weight.
25. Liquid-crystalline medium according to Claim 3, characterized in that it comprises at least one compound selected from the formulae IIIa to IIId:

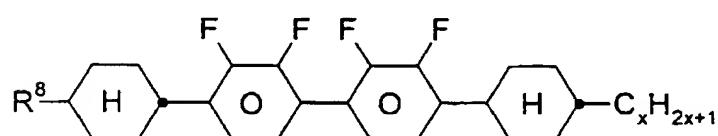
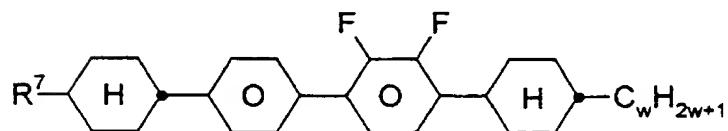


in which

5 alkyl and
 alkyl* are each, independently of one another,
 a straight-chain alkyl radical having
 1-6 carbon atoms.

10 10. Liquid-crystalline medium according to Claim 9,
 characterized in that it comprises at least one
 compound of the formula IIIa and/or at least one
 compound of the formula IIIb.

15 11. Liquid-crystalline medium according to one of Claims
 1 to 10, characterized in that it additionally
 comprises one or more compounds of the formulae



in which

R⁷ and R⁸ are each, independently of one another, as defined for R¹¹, R¹² and R²¹ in Claim 1, and

5 w and x are each, independently of one another, from 1 to 6.

12. Liquid-crystalline medium according to one of Claims 1 to 11, characterized in that it
10 essentially consists of

10-40% by weight of one or more compounds of the formula I1,

15 5-30% by weight of one or more compounds of the formula I2,

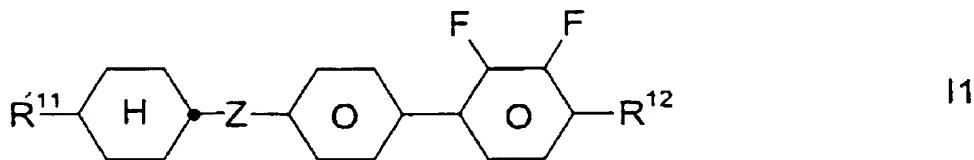
and

20 20-70% by weight of one or more compounds of the formula II.

13. Electro-optical display having active matrix addressing based on the ECB effect, characterized in that it comprises, as dielectric, a liquid-crystalline medium according to one of Claims 1 to 12.

Abstract

The invention relates to a liquid-crystalline medium based on a mixture of polar compounds of negative dielectric anisotropy which comprises at least one compound of the formula I1 and/or I2, [sic]



and at least one compound of the formula I2



in which

R¹¹, R¹², R²¹ and Z are as defined in Claim 1,

and the use thereof for an active matrix display based on the ECB effect.